

Flocculation of Carbon Black in Filled Rubber Compounds. I. Flocculation Occurring in Unvulcanized Compounds During Annealing at Elevated Temperatures

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SYNOPSIS

It has been found that appreciable carbon black flocculation can occur in filled rubber stocks during storage or vulcanization in the absence of shear. The kinetics of this flocculation process were studied by means of low strain dynamic mechanical property and electrical conductivity measurements. The results showed the rate of flocculation to be governed by the type and concentration of carbon black, polymer macrostructure, mixing history, and annealing temperature. A mechanism responsible for the formation of this carbon black network structure was proposed and the resulting changes in the physical properties of vulcanizates prepared from these rubber compounds were elucidated.

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INTRODUCTION

The morphology and properties of carbon black filled rubber compounds are greatly influenced by the state of filler dispersion. In automobile tires, for example, rolling resistance and tread wear and other properties are significantly affected by the dispersion and spatial topology of the reinforcing carbon black. Both are governed by the mixing process in which the carbon black is broken up under shear into individual aggregates and randomly distributed throughout the polymer matrix. However, in analogy with observations made on filler suspensions in oil and other low viscosity media,¹⁻⁴ one may expect that the filler particles will slowly agglomerate on storage of the compound and, given a sufficiently high-volume concentration of filler, would tend to form a continuous matrix. There is evidence for the existence of a partial filler network in rubber compounds based on the work of Payne⁵ and others.^{6,7} It is, however, not clear whether this is due to an incomplete dispersion during mixing or the occurrence of filler flocculation after the mixing step, as

had been suggested by Gerke et al.⁸ and Bulgin⁹ many years ago. Flocculation, if occurring, would counteract, at least in part, the filler dispersion imparted during mixing and cause the viscoelastic properties to be strongly nonlinear and to depend more on strain amplitude as well as strain history.

In this study we examined the degree to which flocculation occurs in unvulcanized rubber compounds under conditions normally encountered during their commercial use. Also investigated was the influence of temperature, carbon black concentration, carbon black type, polymer molecular weight, and mixing history on the kinetics of the flocculation process and the effect it has on the physical properties of rubber vulcanizates.

SAMPLE PREPARATION AND TEST PROCEDURES

A number of polybutadiene rubbers of different molecular weight (Table I), produced by the Firestone Synthetic Rubber and Latex Company, were mixed with three different carbon blacks (N326, N347, N660) varying in aggregate size and structure. The compounds were mixed in a Brabender Plasticorder, cavity volume of 260 cc, at 80 rpm for different time

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Table I Macrostructure of Polybutadiene Elastomers

Polymer	M_n	M_w/M_n
HD25	85000	1.24
HD35	96000	2.1
HD55	105000	2.3
HD75	188000	1.54

periods to achieve a range of carbon black dispersions. Plaques ($160 \times 160 \times 4$ mm) were subsequently prepared by compression molding the compounds at 100°C for 10 min. The mold was then cooled under pressure for about 20 min before it was opened and the sample extracted. To induce different degrees of carbon black flocculation, the plaques were then annealed for time periods of up to 60 min. Vulcanization of the samples at 23°C was then effected by electron beam irradiation using a 1.5 MeV Dynamitron accelerator and doses of up to 15 Mrad.

The macrodispersion of carbon black was measured on freshly cut surfaces with a surface roughness analyzer (Surfanalyzer, Model 2000, Federal Products), and a method developed by Hess (10). A rheometer (Dynastat Viscoelastic Analyzer Model RD-700, Rheometrix) was used to determine the viscoelastic response of the cured rubber samples under cyclic deformation. Annular rings were cut from the vulcanized plaques and clamped between the flat disks of the rheometer. The viscoelastic response, including the storage and loss modulus, was then measured at 23°C and 1 Hz as function of strain amplitude under simple cyclic extension.

EXPERIMENTAL

The level of carbon black flocculation in the vulcanizates was determined from the measurement of the storage modulus E' up to strains of 14%. Figure 1 shows a schematic plot where $\Delta E' = E' (e = 14\%) - E' (e = 0.2\%)$; the excess storage modulus at low strains is taken as a measure of the carbon black network as was first suggested by Payne (5). Any increase in $\Delta E'$ can then be regarded as being caused by carbon black flocculation.

Using this approach, a variety of measurements were made to determine the extent of flocculation occurring in the compounds of this study under a variety of conditions. Figure 2 illustrates the results for a polybutadiene compound containing 50 phr (19 vol %) of N347. As shown, flocculation occurring on

annealing at 150° and 175°C raises $\Delta E'$ to a common plateau level that lies about 80% higher than that of the unannealed sample. At 125°C the flocculation is, of course, slower and did not reach the plateau level after 60 min. The effect of this flocculation induced increase in $\Delta E'$ on the low strain hysteresis is shown in Figure 3, which points to an increase in $\tan \delta$ by more than 11%.

The effect of carbon black concentration on the filler network formation is shown in Figure 4. There is no change in $\Delta E'$ at carbon black levels of 20 phr (10 vol %), which is below the threshold concentration ϕ_{crit} of 13 vol % for N347 black. At 30 phr (14 vol %) there appears to be a small raise in $\Delta E'$ on annealing, but at 50 phr significant flocculation occurs at a rate equal to that shown in Figure 2.

The filler network formation also depends on the type of carbon black used, which is illustrated in Figure 5. There, compounds containing 50 phr of three type of blacks are examined after annealing at 150°C . No change in $\Delta E'$ takes place for N660, a carbon black of large particle size and a threshold concentration of 20 vol %. The increase in $\Delta E'$ is smaller for N326 compared to N347, which has a higher structure. From this, one can conclude that the formation of a filler network occurs only above the threshold concentration predicted by the percolation theory (11) and that it is preferably formed with blacks having a higher structure and smaller particle size.

To investigate the effect of carbon black dispersion on the degree of flocculation, two samples were prepared having the same composition (50 phr N347) but different mixing histories. One sample had a relatively short mixing cycle, the other a long

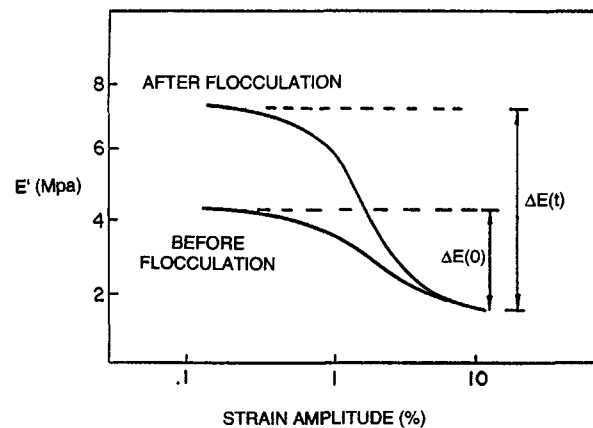


Figure 1 Schematic representation of the strain amplitude dependence of the dynamic storage modulus E' and the effect of carbon black flocculation.

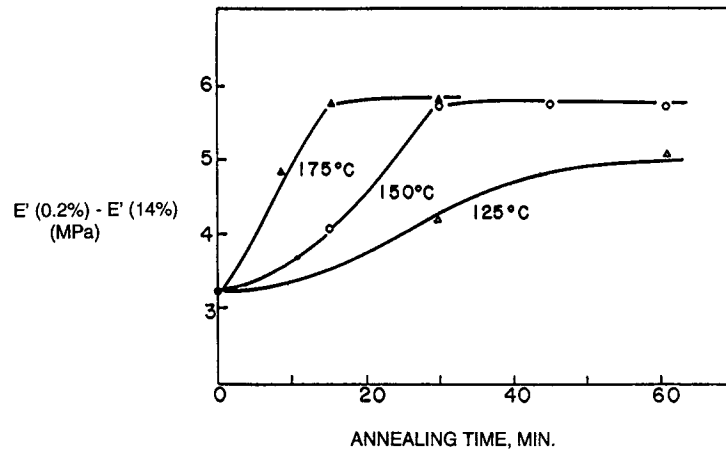


Figure 2 Excess storage modulus changes induced in carbon black filled polybutadiene compounds (50 phr of N347) by annealing at different temperatures.

one that resulted in macrodispersion levels of 46 and 97%, respectively. Figure 6 shows the sample with low carbon black dispersion to have a greater filler network initially, which further increases on annealing at a more rapid pace than for the sample having a higher macroscopic dispersion. The flocculation was completed in 10 min for the short mixed sample vs. 20 min for the long mixed sample. It is thus apparent that the rate of carbon black flocculation also depends on the mixing history of the compounds being investigated.

Finally the molecular weight of the host polymer also affects the flocculation process. This was examined with compositions comprising polybutadienes of different molecular weight and 30 phr N347. Plaques prepared from these compounds were annealed for 30 min at 150°C prior to radiation induced

vulcanization. Figure 7 shows that the rate of carbon black flocculation decreases with increasing molecular weight of the polymer. Such an inverse dependence on molecular weight or indirectly on viscosity would be expected from a diffusion-controlled flocculation process. Figure 8 depicts the $\tan \delta$ changes associated with the $\Delta E'$ changes of Figure 7.

DISCUSSION

The data presented suggests that clusters of carbon black aggregates exist in the compounds of this study which grow on annealing at elevated temperatures. This carbon black structure is responsible for the thixotropic behavior normally observed in the unvulcanized state and the higher initial modulus of the unperturbed vulcanizate at low strains. Our general interpretation of the increase in structure on annealing is that carbon black aggregates are attracted to each other by Van der Waals forces and, hence, given a certain mobility of the carbon black, flocculation of aggregates with preexisting carbon black clusters occurs. Given a certain minimum filler concentration, this will result in the formation of a continuous network.

The kinetics of the flocculation process can then be described by a simple model. To characterize the instantaneous filler network structure in the compound, we first define a dimensionless structural parameter S that describes the fraction of the carbon black structure at any instant while $(1 - S)$ then denotes the part of the network structure present in a nonassociated form that is as individual aggre-

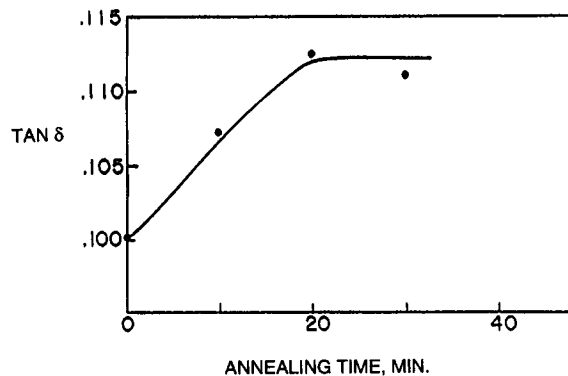


Figure 3 Changes in low strain hysteresis ($\tan \delta$) induced by annealing in a carbon black filled polybutadiene compound.

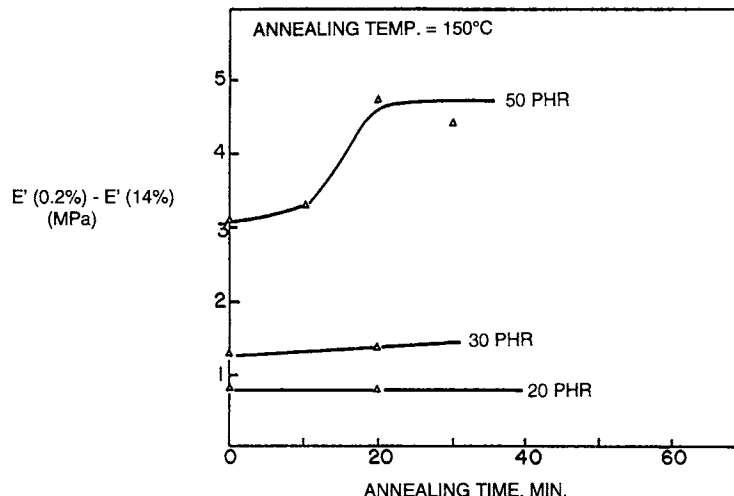


Figure 4 Excess storage modulus changes induced by annealing in polybutadiene compounds comprising different concentrations of N347 carbon black.

gates. Because we assume that the excess storage modulus $\Delta E'$ is a measure of the filler network structure we can thus define S as

$$S = \Delta E'(t) / \Delta E'_R = (E'_0(t) - E'_\omega(t)) / (E'_{0,R} - E'_{\omega,R}) \quad (1)$$

where $S(t = 0) = S_B$ and $S(t = \infty) = S_R = 1$; $E'_0(t)$ and $E'_\omega(t)$ represent the storage moduli at low and high strain amplitudes at an annealing time t ; and $E'_{0,R}$ and $E'_{\omega,R}$ the equivalent storage moduli at $t = \infty$ when a full recovery of the network has been achieved, that is, when all the carbon black aggregates that can flocculate have done so.

Then, the rate equation for the structural recovery of the filler network on annealing for a time t in the absence of shear may be expressed by

$$dS/dt = k_R(S_R - S) \quad (2)$$

Integration then leads to

$$S = S_R - (S_R - S_B)\exp(-k_R t) \quad (3)$$

where k_R is the recovery constant, S_R the network structure recovery at $t = \infty$, and S_B the structure at $t = 0$ when most or all of the structure has been broken down by shear mixing. To test the validity

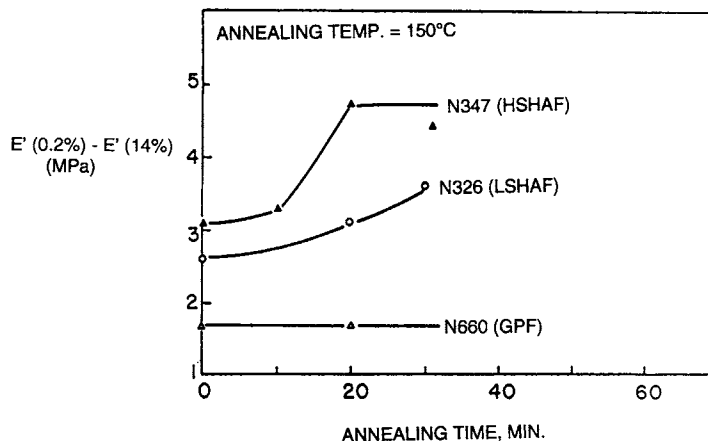


Figure 5 Excess storage modulus changes induced by annealing in polybutadiene compounds comprising 50 phr of different type of carbon blacks.

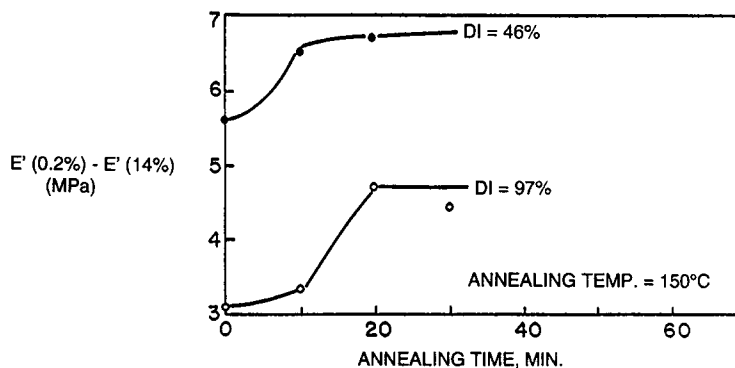


Figure 6 Excess storage modulus changes induced by annealing in two carbon black filled polybutadiene compounds (50 phr of N347) having different levels of macrodispersion.

of this relationship, a semilog plot of $(1 - S)$ against t was made using the data of Figure 2. As one can see from Figure 9, the flocculation data measured at different temperatures is reasonably described by first order kinetics. From this plot, one can readily determine the indicated recovery rate constants for flocculation occurring at different temperatures and calculate an activation energy of 14.5 kcal/mol.

The carbon black network formed by flocculation is, of course, readily disrupted by further mixing, and one can describe the dynamics of the breakdown and recovery process by the graph shown in Figure 10. During initial mixing of the compound by a blending of the elastomer with carbon black, the structure parameter S is not defined at first, due to the compositional inhomogeneity of the sample. However, once the carbon black is randomly distributed, the carbon black network can be readily measured as a function of time by removing samples from the batch and measuring $\Delta E'$ after molding

and vulcanization. One then observes that S approaches a value S_B that represents steady-state conditions at which the rate of breakdown of any carbon black agglomerate is equal to the rate at which they reform by flocculation. S_B will depend on the rate of structure breakdown and presumably decrease with increasing shear rate imposed on the sample during mixing. It is, however, not possible to determine the value of S_B from the above-described measurements on annealed plaque samples because the structure parameter S measured at $t = 0$ is unlikely to correspond to the one that represents the carbon black structure at the time when mixing of the compound was stopped. This is because considerable time elapsed between that moment and the time when the mixed compound had been molded into a plaque and was subsequently vulcanized by radiation cross-linking. We thus have to assume that some flocculation will have occurred during that time interval and that the structure pa-

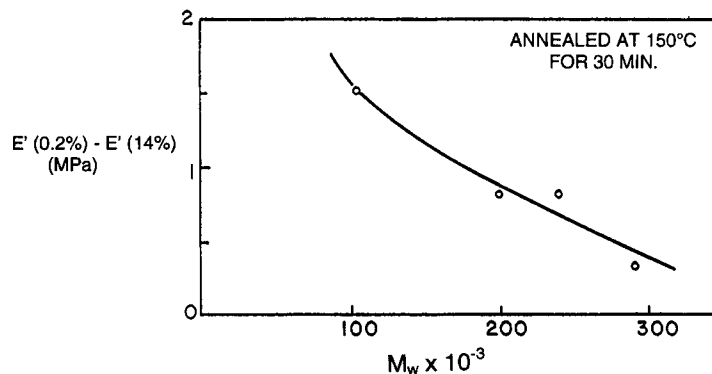


Figure 7 Excess storage modulus changes induced by annealing at 150°C for 30 min in compounds comprising polybutadienes of different molecular weight and 30 phr of carbon black (N347).

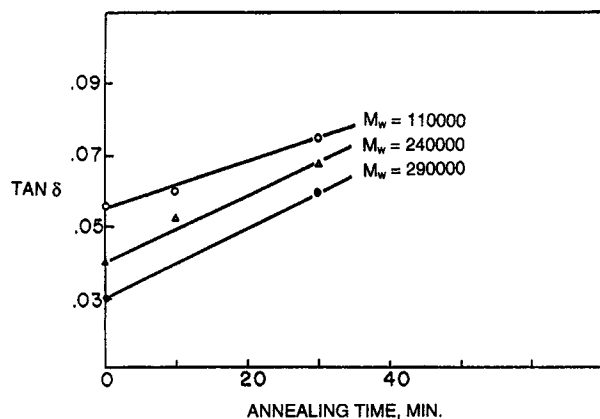


Figure 8 Changes in low strain hysteresis ($\tan \delta$) induced by annealing of compounds referred to in Figure 7.

parameter S measured prior to the annealing step is thus larger than the one that existed in the sample at the end of the mixing process.

As shown in Figures 2–7, an annealing of the compounds at elevated temperatures promotes the flocculation of carbon black, and S eventually approaches a value S_R at which all the carbon black that can be added to the network has been incorporated. If at that time or, for that matter, at any time prior to reaching S_R , the compound is again exposed to shear mixing, the carbon black structure is again broken down quickly because $k_B > k_R$. Values of k_B ranging from 0.2 to 1.4 min^{-1} were measured at different mixing temperatures and rotor speeds (12).

As to the mechanism of the network forming process, we assume that some contacts may exist between individual carbon black aggregates at the end of the mixing process, particularly if the filler concentration exceeds the threshold volume fraction Φ_{crit} at which randomly dispersed particles touch to form an infinite contiguous chain. That concentration was predicted by percolation theory^{11,13–15} and measured on a number of polymer systems. Data for two rubbers and carbon blacks of different size and structure¹⁶ is shown in Figure 11. For randomly incorporated spheres a Φ_{crit} of 0.3 is observed, but that value can be considerably lower for nonspherical particles and nonrandom dispersions of the aggregates in the host matrix. Φ_{crit} is predicted by the following equation¹⁷

$$\Phi_{\text{crit}} = 1/(1 + 4\nu\rho) \quad (4)$$

where ρ is the density of the filler particle and ν is the void space, which in turn can be determined by dibutylphthalate (DBP) absorption.¹⁸ Using ν values

for different carbon blacks ranging from 1.25 for acetylene carbon black to 0.37 cm^3/g for low structure N880 carbon black, Φ_{crit} values of 0.1–0.3 are predicted by Eq. (4). Figure 11 compares these predicted values with the measurements of Kraus and Svetlik.¹⁶ As one can see, Φ_{crit} is strongly influenced by the structure of the carbon black aggregates that manifests itself by an anisometric and often highly branched assembly of fused primary particles. Predicted ϕ_{crit} values and those measured for poly(butadiene-*co*-styrene) rubber (SBR) are not in good agreement. The closer fit with the data on natural rubber (NR) may be fortuitous because the lower ϕ_{crit} reported for NR may be attributed to an exclusion of carbon black aggregates from small crystallites formed by a mixing induced straining of the rubber molecules. This would present a *de facto* increase in filler concentration in the amorphous phase.

The number of contacts between carbon black aggregates in a host matrix below and above Φ_{crit} can be predicted by percolation theory. There, the assumption is made that a large lattice with N sites is randomly filled with carbon black aggregates placed in “allowed” sites. If the concentration of such allowed sites x is small, the sites occur singly or in small isolated clusters of adjacent sites. As x increases, larger clusters occur and the mean size of a cluster increases monotonically. Eventually, these clusters begin to merge as x approaches x_{crit} and an

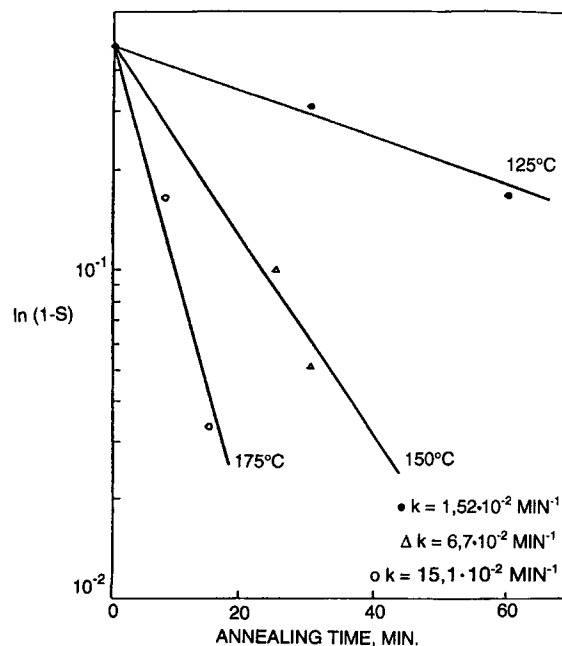
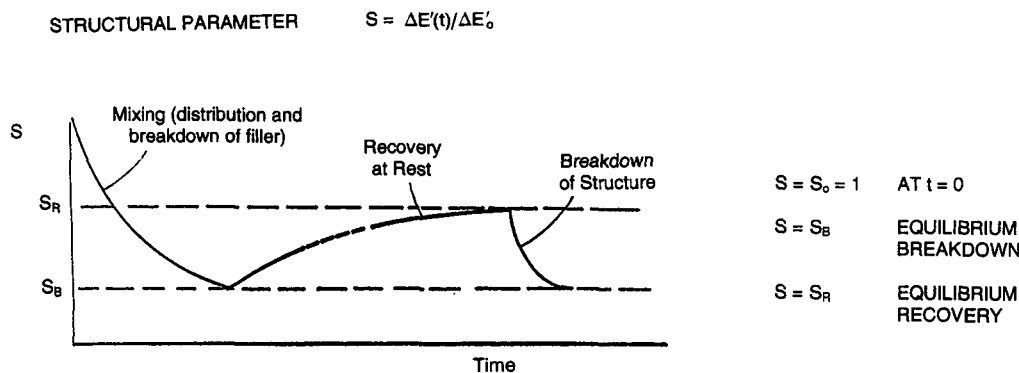


Figure 9 Rate of carbon black flocculation at different temperatures.



RECOVERY PROCESS:

$$\frac{ds}{dt} = k_R(S_R - S)$$

$$S - S_R = (S_B - S_R) e^{-k_R \cdot t} \text{ WITH } k_R = A(T) \exp\left(\frac{-E}{KT}\right)$$

Figure 10 Schematic representation of structural parameter S as function of time during the mixing of a carbon black filled compound, on annealing in the absence of shear, and during subsequent shear mixing.

infinite chain structure pervading the matrix is formed. As $x > x_{crit}$ the ratio of the number of sites in this infinite chain N_{chain} to the number of occupied sites in the lattice N_T at first increases by a simple power law dependence on $(x - x_{crit})^n$, and then tends toward a sharply defined function of x (graph A of Fig. 12).

As was suggested by Bueche,¹⁹ this cluster forming process can also be described by the theory of gel formation involving the random cross-linking of polymers. Using this approach, the number fraction

of carbon black clusters comprising z interconnected aggregates can be estimated near x_{crit} by

$$n(z) = \rho/m_0(2\pi z^5)^{1/2} \tag{5}$$

where m_0 is the mass of an aggregate and ρ is its density. A contiguous infinite molecular chain is formed at the gel point when one cross-link is introduced per weight average molecule. The increase in gel formed on further cross-linking, as shown in graph B of Figure 12, is analogous to the increase

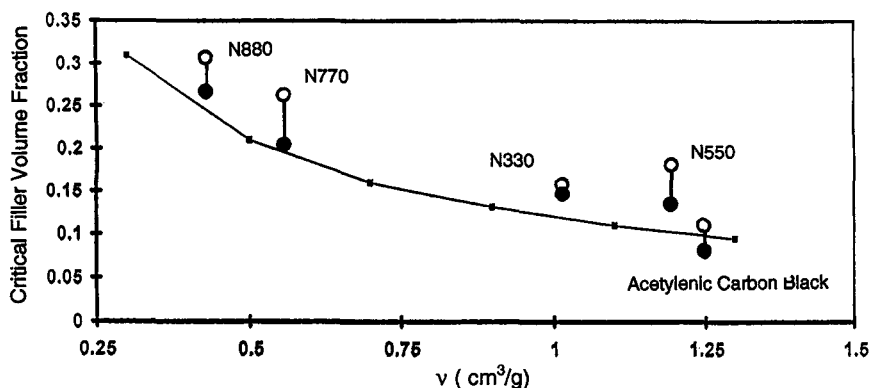


Figure 11 Critical filler volume fraction ϕ_{crit} as a function of carbon black structure as measured by DBP absorption. Solid line represents data calculated from Eq. (4). Open and filled circles show data for SBR and NR stocks.¹⁶

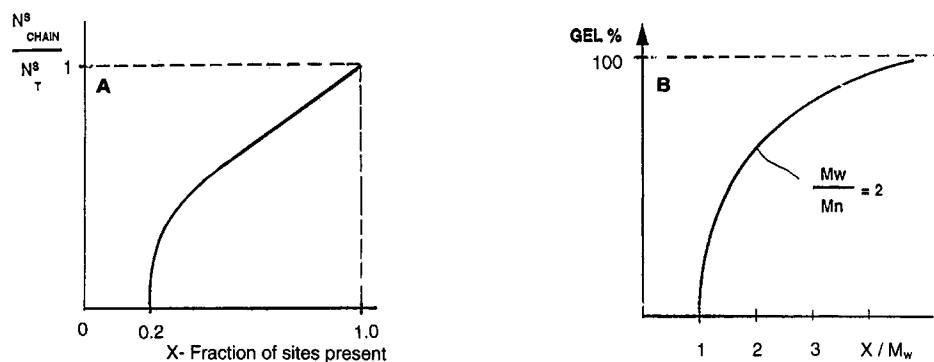


Figure 12 Carbon black network formation predicted by percolation and polymer gelation theories. Graph A: Site percolation probability for 3D lattice plotted as a function of the fraction of sites present. Graph B: Gel growth as function of cross-links per weight average molecule for the case of random molecular weight distribution of polymer chains.

in N_{chain}/N_T as a function of x predicted by the percolation theory (graph A). Both approaches, however, look only at the carbon black chain formation from a static point of view, that is, they predict the occurrence of contacts based on proximity and random packing arguments.

To explain the results of our experiments, other points need to be taken into consideration. First and foremost, we postulate that the number of contacts between carbon black aggregates in the compounds of this study is not a uniquely defined parameter depending only on Φ_f , but is also affected by the flow during mixing and by any later storage or annealing of the compound in the unvulcanized state. This can be understood from the following arguments.

Shear induced collisions of carbon black aggre-

gates occur frequently during mixing, but the average time period in which two such aggregates are in contact is expected to be very short. Consequently, the probability that during that short time period one of the two aggregates is also in close contact with a third or fourth aggregate is relatively small because it inevitably involves joint probabilities and, hence, the product of several stereometric factors. Therefore, one would expect only a relatively small concentration of carbon black clusters to exist during mixing, certainly a much smaller concentration than the one predicted for a given Φ_f from percolation theory. Once shear mixing stops, contact formation should be facilitated by the attractive forces acting on two aggregates in close proximity and the limited mobility of the aggregate in the highly viscous host

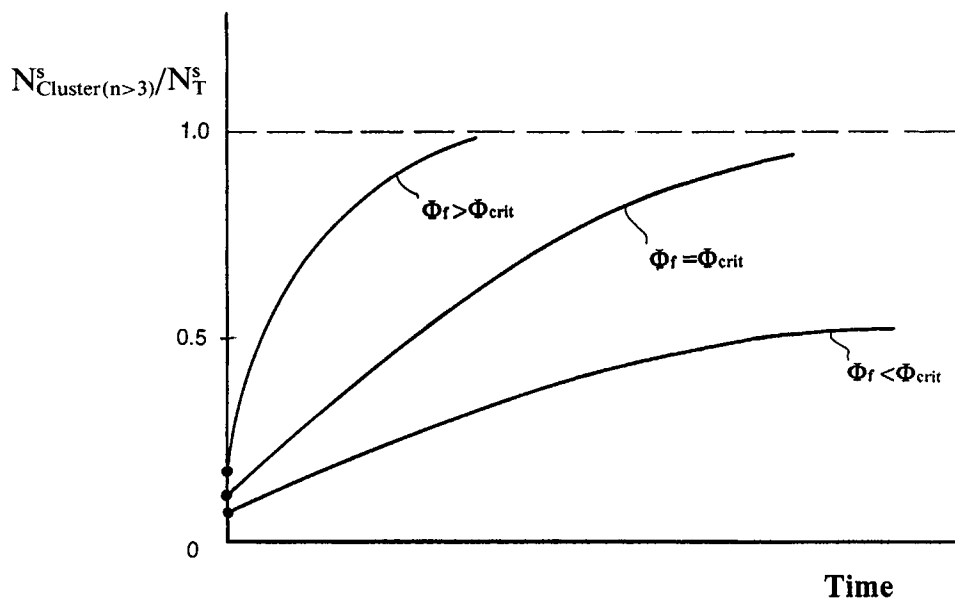


Figure 13 Schematic representation of anticipated flocculation induced carbon black cluster formation during annealing of compounds with different filler volume fractions.

matrix. Such mobility could be generated initially by a nonaffine recovery of stresses induced in the compound by the mixing process. This motion will cease after time periods exceeding the longest relaxation time of the polymer molecules and any further motion will then be based on Brownian diffusion.

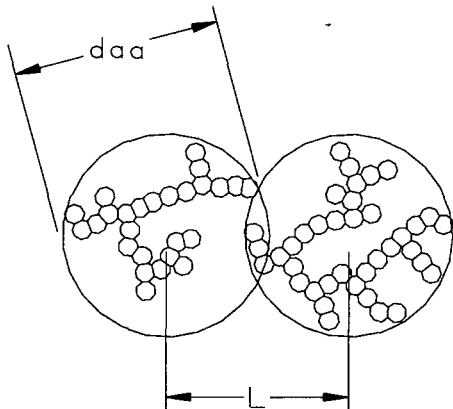
Let us now estimate the time needed for carbon black aggregates to diffuse over the required distance to make contact with another aggregate. The distance carbon black aggregates would have to move depends, of course, on the average size and shape of the carbon black particles and the volume fraction of filler in the composite. For spherical particles of radius a distributed in a cubic arrangement, the distance between the centers of the spheres L can be readily determined from

$$L = (4a^3\pi/3\Phi_f)^{1/3} \quad (6)$$

where Φ_f is the volume fraction of filler. Considering that carbon black aggregates are made up of many primary particles fused together, and taking into account the effective volume fraction of filler Φ_{eff} , Wang et al.²⁰ calculated the interaggregate distance in filled rubber compounds. Rearrangement of their equation and assuming random packing leads to the following equation for L , the distance between the centers of two aggregates

$$L = 0.86\Phi_{\text{eff}}^{-1/3}d_{\text{aa}} \quad (7)$$

where $d_{\text{aa}} = 6000 N_p^{0.436}/\rho S$ and $\Phi_{\text{eff}} = \Phi_f\beta$. In this equation d_{aa} is the aggregate diameter and N_p the number of particles/aggregate. For the case of the compound referred to in Figures 2 and 3 (50 phr of N347) for which $\Phi = 0.21$, $S = 87$, $N_p = 102$, and $\beta = N_p^{0.305} = 4.1$, we obtain an aggregate diameter of 2860 Å and $L = 2187$ Å. $L < d_{\text{aa}}$ indicates that the spatial arrangement of the aggregates should be as outlined below, with a partial overlap of the outer aggregate circles.



In this case, a carbon black aggregate would have to diffuse a distance of less than an aggregate radius to contact another aggregate. A rough estimate of the time required for diffusing such distance can be made from the diffusion constant D , using Stokes' equation for spherical particles

$$D = x^2/2t = kT/(6\pi\eta a) \quad (8)$$

where k is the Boltzmann constant, η the viscosity, and a the radius of the particle. For $\eta = 4 \times 10^5$ P and an assumed distance of 1000 Å we estimate the time to diffuse such distance to be about 12 min, which is well within the annealing times of the experiments conducted. In reality, of course the carbon black aggregates in a given sample differ somewhat in size and shape and are, at best, randomly distributed in the compound. Consequently, one should expect a wide distribution of interparticle distances and thus also of diffusion times for contact formation.

Considering all the above, the following arguments, qualitatively illustrated in Figure 10, can be made about the flocculation process. The starting point for the distribution of carbon black in a compound is represented by the end of the mixing process ($t = 0$) that determines the overall position of the carbon black aggregates relative to each other. At that time, one should expect few contacts between more than two aggregates and thus no significant amplitude dependence of $\Delta E'$. After that, motion will be induced in the matrix by stress relaxation and Brownian diffusion, which will bring aggregates in close proximity to other aggregates. When that happens, attractive van der Waals forces will pull the two aggregates to within an equilibrium distance²¹ and, in the absence of any external force, will non-reversibly bond the two aggregates to each other. This process, occurring throughout the matrix, will lead to the formation of larger clusters and given a sufficiently large volume fraction of carbon black, to the establishment of a contiguous infinite network.

Figure 13 shows schematically the rate of flocculation for different filler concentrations. In the case $\phi_f > \phi_{\text{crit}}$ the interaggregate distance is small indeed, and thus the network will be formed quickly, certainly in a shorter time than was required to prepare the sample for the annealing experiments conducted in this study. We thus assume that the $\Delta E'(t = 0)$ value of Figure 2 is attributable to a contiguous network extending throughout the sample and that the further increase in $\Delta E'$ on annealing is caused

by the attachment of remaining isolated aggregates to this network. After annealing the sample at 175°C for 20 min, $\Delta E'$ reaches a plateau. Presumably all the aggregates have been incorporated in the network by that time.

For $\phi_f = \phi_{crit}$ the events are expected to be similar except that, owing to the larger interaggregate distance, the flocculation induced cluster formation proceeds at a much slower pace.

Finally, if $\phi_f < \phi_{crit}$, the time for cluster formation will be even longer and no infinite network will be formed at all.

The flocculation process should also affect ϕ_{crit} to some degree. Unlike the permanent random placement of aggregates in a lattice, as is assumed by percolation theory, flocculation provides a means to bridge vacant sites required for the formation of a larger cluster or an infinite network. This flocculation induced deviation from a random aggregate distribution should allow network formation to occur over extended time periods at somewhat lower carbon black concentration than would be predicted by percolation theory.

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